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TECHNOLOGY FOR THE HYDROMETALLURGICAL PROCESSING OF A COMPLEX MULTICOMPONENT SULFIDE-BASED RAW MATERIAL

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An analysis of the methods currently used for the metallurgical processing of polymetallic middlings from the beneficiation of sulfide ores shows that the oxidant which is the most promising for use as an agent to leach the middlings is nitric acid. A technology is developed to process hard-to-decompose middlings with the use of nitric acid.

Keywords: *multicomponent sulfide middlings, nitric-acid leaching, processing technology.*

Status of the metallurgical processing of polymetallic middlings obtained from the beneficiation of complex sulfide ores. Over the last few decades, an increasing percentage of the raw materials processed by the metallurgical industry have been out-of-balance, oxidized, and mixed ores based on sulfides. The use of such materials is related to the fact that the reserves of the most accessible and most easily mined minerals shrink each year. With the transition to the mining of deeper-lying ore beds, problems have arisen in connection with the reduction in their content of metals and an increase in the percentage of hard-to-concentrate ores. These problems are typical not only of various deposits, but also of individual seams due to their nonuniform morphological composition and crystalline structure [1].

The above-mentioned factors have an adverse effect on the performance of concentration plants: the quality of the concentrates decreases, there are rises in reagent use, energy costs, and expenditures on equipment maintenance, the volume of circulating flows increases, etc. These changes ultimately lead to an increase in production costs and a decrease in productivity.

To ensure high performance indices for the process of separating collective concentrates into zinc, copper, and lead concentrates, plants are adopting the practice of removing small volumes of collective semifinished products or middlings from the concentration line (at certain points along the line); the middlings are complex sulfide compounds that cannot be separated by flotation [2].

Existing pyrometallurgical methods are proving to be ineffective for processing such low-grade raw materials – the cost of obtaining the product turns out to be higher than its market value. The use of pyrometallurgical methods also creates environmental problems, thus incurring numerous fines and penalties [3].

In light of the foregoing, it is important to develop and introduce new hydrometallurgical technologies that are more promising from both the environmental and economic standpoints.

Studies were performed at Ural Federal University (MTTsM Department) to develop a leaching technology that uses nitric acid to break down multicomponent sulfide ores which are difficult to concentrate by traditional methods. The use of nitric acid as the oxidizing agent is distinguished by the high rates of the accompanying chemical reactions and the completeness with which metals are recovered in the solution with low reagent use.

We performed balance tests to determine the optimum parameters for individual stages of a technology designed to process multicomponent sulfide semifinished products (see Fig. 1).

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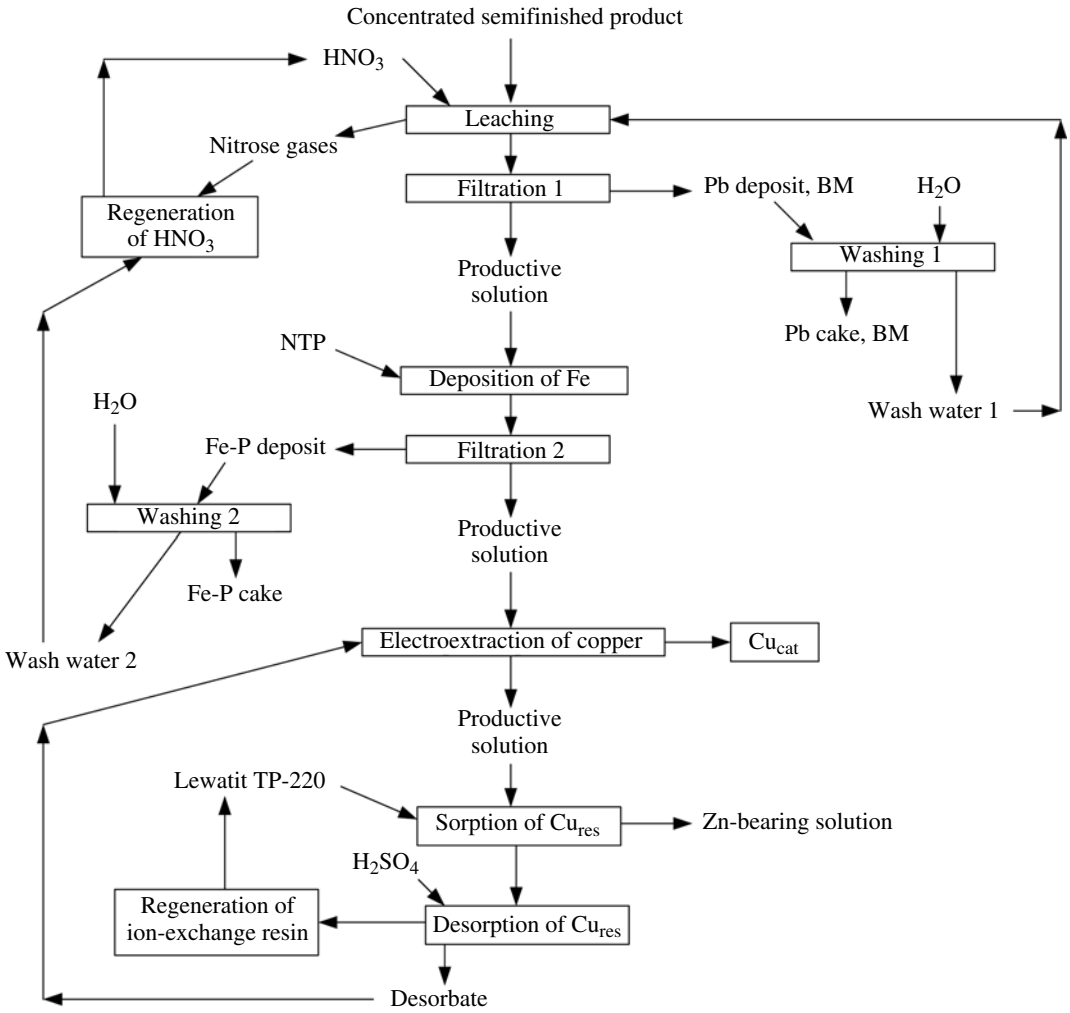

Fig. 1. Flow chart for processing multicomponent sulfide semifinished products.

The raw materials used for the studies was a semifinished product obtained from the Maikain deposit (in Kazakhstan). This material is a multicomponent sulfide concentrate that cannot be processed by selective flotation. The chemical composition of the flotation concentrate (in terms of the dry raw materials) is as follows: Cu 6.10; Zn 8.70; S 53.00; Fe 28.80; As 0.48; Pb 1.11; Au (g/ton) 11.50; Ag (g/ton) 81.00; Ca 1.24; Mg 0.48.

The semifinished product was delivered for the leaching operation, which also involved the use of 57% nitric acid and water used to wash the leached product (L:S = 5.1). Fresh nitric acid was used in the first cycle, while a substantial part of the oxidant used in the subsequent cycles was nitric acid obtained in the regeneration stage.

The process took 2 hours. The pulp that was obtained was sent to the filtration stage, which yielded a productive solution that was dispatched to the next processing stage and a deposit which contained undissolved components of the raw material (mainly lead), compounds from the country rocks, and noble metals that can be recovered later by conventional methods. The deposit was washed, dried, and weighed and the wash water was returned to the leaching stage.

The nitrose gases formed in the reaction of the nitric acid with the middlings were directed to an absorption column that was irrigated with wash water from the iron precipitation stage and was supplied with air to oxidize the gases to higher oxides of nitrogen. The nitrose gases and water vapor were subjected to preliminary cooling and condensation in a cooler-condenser.

TABLE 1. Summary Balance of the Proposed Flow Scheme

Input item, kg		Output item, kg	
Copper			
Middlings	55.5	Pb cake, BM	2.2
		Fe-P cake	1.2
		Cathodic deposit	52.1
Total	55.5	*Total*	55.5
Zinc			
Middlings	79.1	Pb cake, BM	1.3
		Fe-P cake	1.7
		Zn-bearing solution	76.1
Total	79.1	*Total*	79.1
Iron			
Middlings	262.0	Pb cake, BM	7.7
		Fe-P cake	254.3
Total	262.0	*Total*	262.0
Sulfur			
Middlings	482.0	Pb cake, BM	33.5
Sulfuric acid for desorption	8.5	Fe-P cake	23.4
		Zn-bearing solution	433.5
Total	490.5	*Total*	490.5
Water			
Middlings	100.0	Pb cake, BM	22.7
$HNO_{3\ conc}$	571.7	Gas phase in HNO_3 regeneration	581.0
For washing 1	540.0	Fe-P cake	63.9
For washing 2	1819.0	Zn-bearing solution	2494.0
H_2SO_4 for desorption	130.9		
Total	3161.6	*Total*	3161.6

The regenerated nitric acid was returned to the leaching stage at the “head” of the production line. The productive solution obtained at the leaching stage was sent off to separate iron in the form of insoluble complexonates of the composition $Fe_3H_3(ntph)_2$. To accomplish this, we also supplied nitryl trimethylene phosphoric acid (NTP) in a metal:ligand ratio equal to 3:2.

The reaction was accompanied by the momentary precipitation of a white cottony precipitate. However, to allow precipitation to proceed further to completion, the pulp was held for 1 hour while being continuously agitated. The filtered iron-bearing precipitate was washed, dried, and weighed.

The iron-phosphorus cake that was obtained can be used as a semifinished product at ferrous metallurgy plants to make a valuable iron-phosphorus master alloy.

After the iron precipitation stage, the productive solution was dispatched to the next processing operation – the electrical extraction of copper. This process was carried out in an open electrolysis cell with forced circulation of the electrolyte.

The cathodes were made of an acid-resistant stainless steel, while the anodes were made of platinum-coated titanium.

The electrolyte obtained at the electrodeposition stage contained 20–25 g/dm^3 copper. Its acidity was on the order of 100 g/dm^3. The duration of the process was 48 hours.

Cathode current density decreased from 200 to 50 A/m^2 as the electrolyte was depleted of copper. Voltage in the bath was kept within the range 1.8–2.4 V. Current efficiency was 91–93%.

The cathodic precipitate was washed and weighed at the end of the process.

To remove the remaining copper from the depleted (to 1 g/dm^3) solution, sorption was performed on ion-exchange resin Lewatit Monoplus TP-220. The resin was in the fully regenerated H-form (expanded and hydrated).

The studies were conducted in the static regime. The resin and solution were kept in contact with one another for three days and periodically mixed. The saturated resin was then separated from the solution and washed with distilled water to the neutral-reaction point.

Copper was desorbed from the resin by sulfuric acid with periodic mixing. The concentration of sulfuric acid was 180 g/dm^3. The resulting eluent was sent to the copper electroextraction stage.

The copper-depleted solution, containing 45–50 g/dm^3 zinc, can be recycled by standard zinc technology.

The results of the completed tests were used to construct the summary material balance of the proposed flow scheme (see Table 1). The calculations were performed for 1000 kg of dry middlings.

Conclusions

1. The findings of studies made of the processing of multicomponent sulfide-based intermediate products have refined and augmented the results obtained from determining the optimum parameters of the production process.

2. The results made it possible to calculate the material balance of the process based on the individual operations that are performed, as well as to determine the consumption of the reagents and the quantities of the semifinished and finished products.

3. Plans are being made to use the data that were obtained to evaluate the environmental-economic effectiveness of the technology that has been developed for processing multicomponent sulfide middlings.

REFERENCES

1. S. S. Naboichenko, L. P. Ni, Ya. M. Shneerson, and L. V. Chugaev, *Autoclave Hydrometallurgy of Nonferrous Metals* [in Russian], UGTU-UPI (2002).
2. V. V. Belikov, "Processing hard-to-concentrate polymetallic ores by combination-type concentration methods," *Obogashch. Rud*, No. 3, 22–24 (1994).
3. S. E. Klyain, S. V. Karelov, and V. I. Deev, *Nonferrous Metallurgy: Ecology and Economics* [in Russian], Ekaterinburg, UGTU-UPI (2000).